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A numerical study of supercritical water oxidation of phenol

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Abstract

Supercritical water oxidation has attracted attention of many researchers ever since the idea has emerged about three decades ago as a promising technique in the waste management industry. Providing more details about the behavior of a supercritical water oxidation system under various operating conditions and extending available data can greatly assist more accurate and reliable design of such systems. In this study, oxidation of phenol in supercritical water has been modeled as a plug flow reactor. The variations of main system parameters such as temperature and waste concentration along the reactor have been calculated. The numerical model predictions have been compared with available experiments and good agreement has been obtained for steady state operation conditions. In addition, the responses of the numerical model to some unsteady events, such as sudden increases of mass flow rate or fluid inlet temperature have been examined. These situations may possibly occur due to malfunction of various components of the system. It has been shown that the design temperature of the reactor with usual consideration of the safety factors supports the probable range of sudden alterations.

Keywords: Supercritical water; Oxidation; Phenol destruction; Reactor modeling; Non-stationary.

1. Introduction

When the pressure and temperature of water reach close to the critical point, the properties and behavior of water vary greatly when compared to normal pressures and temperatures. Supercritical water oxidation (SCWO) is based on the properties of supercritical water. In this process, the dielectric constant of water decreases to a point of kinship to nonpolar organic solvents such as benzene. Therefore, nonpolar organic compounds and gasses such as oxygen become completely soluble in supercritical water. During the oxidation process of supercritical water, nonpolar organic compounds react with an oxidant, most commonly oxygen, in a single phase reaction producing carbon dioxide and water. The availability of high concentration reactants as well as the lack of mass transfer between phases resulting in faster reactions is advantages brought about by the single phase environment of this process. Chlorine heteroatoms, sulfur, and phosphorous present in organic wastewaters lead to the production of inorganic

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hydrochloric, sulfuric, and phosphoric acids respectively. The nitrogen present in the inorganic compounds results in the production of N_2 and small amounts of N_2O [1].

There are many advantages of oxidation at higher temperatures compared to lower temperatures. For example, higher temperatures cause faster reactions. In addition, the temperatures used in SCWO are considerably lower than the temperature required for producing ash, and no polluting gases such as NO_x and SO_x are produced. The efficiency of destroying organic wastes in SCWO is similar to that of incineration, while SCWO does not lead to dangerous radiation [2]. The operating conditions of supercritical water oxidation are at a temperature of 500-700 °C and a pressure of 24-50 MPa. The time it takes for the complete reaction to occur seldom exceeds several minutes [1]. Therefore, organic carbon is transformed into oxidized carbon rather quickly. The duration of this process depends on the specific operating conditions and the organic compound which is to be oxidized [2].

The efficiency of destruction of wastes in the process of supercritical water oxidation also known as hydrothermal processing is often more than 99.99 percent. Therefore the exit stream of the process can be released into the environment without the need of any further treatment.

The use of supercritical water oxidation for destroying and breaking down various industrial stream wastewaters, in particular toxic and hazardous streams has been increasing due to its many advantages. So far streams containing phenol [3-7], 2,4-dinitrophenol, formic acid, thiodiglycol, methylphosphonic acid [7-10], methanol [5, 11], fenuron, benzene, PET, aromatic compounds [12-15], aniline [16, 17], glycine [17], 2,4-sichlorophenol, urea, [18, 19], ethylene diamine tetra acetic acid, halogenated hydrocarbons, aliphatic nitro compounds, biomass, O-dichlorobenzene, textile wastewater [20-25], toxic organic wastewaters, 2,4,6-trinitrotoluene, wastewater from acrylonitrile manufacturing plant, oily sludge, heavy metals in medical waste incinerator fly ash, 2-chlorophenol, glucose solution, sodium 3,5,6-trichloropyridin-2-ol, municipal sludge and landfill leachate [26-35] have been processed with this powerful technology.

Some researchers have studied the mechanisms and kinetics of the oxidation of various compounds in supercritical water oxidation conditions. Some of these compounds include phenol, 2-chlorophenol, cutting oil wastes, dimethyl methylphospate, methanol, methylamine, quinoline, petroleum derived aromatic and aliphatic hydrocarbons and ethanol [36-44]. The rate of heat transfer of supercritical fluids is also different from fluids in normal conditions. Heat transfer to supercritical fluids has been the area of study for many researchers. Numerous numerical models and semi-empirical models which have been suggested for heat transfer to supercritical fluids have been utilized when modeling supercritical oxidation systems [45-47]. As a result, extensive information is available on the reaction of numerous compounds in various conditions of supercritical water oxidation. These conditions are dependent on the type of reactor as well as the reacting compounds.

Being aware of the behavior of a hydrothermal oxidation reactor is vital for improving the safety and efficiency of the unit. For example in order to prevent irreversible damage to the reactor and assure the safety of the process, the control of temperature is imperative. However due to the high pressures of the process, obtaining the physical data inside the reactor is difficult. Hence no experimental data exists for these conditions. In addition, experimentation on a reactor, especially in transient and non steady state conditions, can prompt serious risks for the reactor itself.

A mathematical model can be considered a solution for this problem. In addition, after initial evaluation, a model can prove useful for scaling up reactors for industrial uses. A model is also capable of providing more information than experimental results as well as predicting possible problems caused by the temperature variations in the reactor. The development of simulation tools has an important role in scaling up processes and acquiring knowledge about the changes of the fluid within the reactor. Computational fluid dynamics and process simulation are significant tools for designing and optimizing such chemical processes. Most available models consider the flow in steady state conditions and use commercial software's such as FLUENT and ANSYS

CFX in order to discover the temperature and concentration profiles inside reactors [48-50]. The numerical modeling, therefore, as well as experimental studies strives to determine the final conversion ratio, the temperature profile along the reactor, or kinetic parameters of the reaction. Meanwhile for industrial equipment and experimental samples, understanding the behavior of the reactor in abrupt conditions is paramount. The numerical model developed in the current study considers unsteady as well as steady state conditions. The details of the model are explained in the following sections.

2. Modeling Procedure

In this study, a numerical model for the prediction of the temperature and concentration gradients under various flow conditions has been developed. To accomplish this, a plug flow reactor has been modeled under the wall boundary conditions with and without (adiabatic) heat transfer to the surrounding. Then the numerical model is proposed for unsteady conditions and the results with respect to possible applications have been discussed. The sudden changes in the fluid inlet temperature or mass flow rate to the reactor are considered as examples of unsteady flow conditions. The explanations about the computational scheme used to model the process and the mathematical equations describing the physical and chemical events within the reactor are described below.

2.1. Flow Specifications and Assumptions

The geometry of the study is a tubular reactor. Due to the high mixing and uniformity of temperature and pressure, and the low corrosion, the diameter of the reactor is considered to be small and the regime of the flow to be turbulent. The simplest model for explaining these conditions is a plug flow reactor. In an ideal reactor, there is no axial mixing, and the fluid elements spend an equal duration of time in the reactor. Therefore the following assumptions are made:

a. Diffusion of species and energy as well as turbulent mixing processes along the flow direction are negligible. In other words axial diffusion is slow compared to convection.

b. At any cross section of the reactor, the temperature, composition and pressure are uniform. In other words, radial mixing is very fast.

c. The radial velocity profile is considered flat.

Therefore a one dimensional model can be used. At first, a steady state model needs to be derived. To better validate the precision of the numerical model, phenol has been used as the waste substance. That is because a good amount of experimental data on the supercritical oxidation of phenol is available in the literature.

2.2. Fluid Properties

There are several components inside the reactor. In general, in order to find the properties of mixtures, the effect of each component must be known. Since the dominant bulk of the fluid inside the reactor is water and the pure water which is the product of the reaction increases in the course of the flow, the properties of the fluid are considered to be that of pure water. This assumption has also been used by other researchers [48, 51-53]. The NIST, National Institute of Standards and Technology are used to estimate water properties.

2.3. Kinetic Parameters

The mechanism of the oxidation of phenol involves many stages and intermediate species [36]. The reaction in its general form is expressed as:

$$C_6H_6O + 7O_2 \rightarrow 3H_2O + 6CO_2 \qquad 1$$

From the kinetics point of view, based on Arrhenius' law, the rate of reaction is dependent on the temperature. In turn, the speed of the reaction is dependent on the concentration of the reactants namely the wastes and oxygen. Therefore:

$$r = K\exp\left(\frac{-E_a}{RT}\right) C^m_{C_6H_6O}\, C^n_{O_2} \qquad 2$$

where K is the pre-exponential factor, E_a the activation energy, R the gas constant, T the temperature, $C_{C_6H_6O}$ the phenol concentration, C_{O_2} the oxygen concentration and m and n the reaction order with respect to waste (phenol) and oxygen, respectively. Some kinetic parameters available in the literature for oxidation of phenol have been briefly reviewed in Table 1.
Therefore,

$$r = K\exp\left(\frac{-E_a}{RT}\right) C_{C_6H_6O} \qquad 3$$

Table 1
Kinetics parameters for oxidation of phenol.

	K (s^{-1})	E_a ($kJ.mol^{-1}$)	m	n	Reference
A	$10^{1.34\pm.77}$	39.2 ± 10.7	1	0	[54]
B	1970	60.8	1	0	[55]

Since the entire reactor is at a supercritical state, the oxidant is completely mixed within the supercritical water, the process is turbulent, and the diameter of the oxidant injection pipe is small, it is assumed that upon entering the reactor the oxidant is immediately mixed and reacts all across the reactor [53].

2.4. Conservation Equations

The simplified governing equations for a compressible Newtonian fluid upon taking into consideration the above-mentioned assumptions are as follows:
Conservation of Mass (Continuity)

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho u) = 0 \qquad 4$$

where t denotes time, x, the reactor length, u, the axial fluid velocity and 5, the fluid density.
Conservation of Momentum (Navier-Stokes)

$$\frac{\partial(\rho u)}{\partial t} + \frac{\partial}{\partial x}(\rho u u) = \frac{\partial \tau_{xx}}{\partial x} - \frac{\partial p}{\partial x} + S_u \qquad 5$$

where τ_{xx} denotes the stress tensor, p, the static pressure and S_u, the volumetric forces such as ρg.

Conservation of Energy

$$\frac{\partial(\rho h)}{\partial t}+\frac{\partial}{\partial x}(\rho u h)=\frac{\partial P}{\partial T}+u\frac{\partial P}{\partial x}+\varphi+S_h \qquad 6$$

where *h* is the enthalpy of the mixture, φ specifies the positive-definite viscous dissipation function, and S_h denotes the source term (for example, because of the reaction heat or heat loss) and is expressed as:

$$S_h=-W_{lost}-r\Delta_r H \qquad 7$$

where $\Delta_r H$ represents the heat of reaction and *r* the reaction rate. W_{lost}, is the heat loss by the reacting medium. The volumetric heat loss according to Newton's law is expressed as:

$$W_{lost}=\frac{H}{d}(T-T_{ext}) \qquad 8$$

where *H*, T_{ext} and *d* denote the overall heat transfer coefficient with the surroundings, the external temperature, and the internal diameter of the reactor, respectively.

Conservation of Species

$$\frac{\partial}{\partial t}(\rho y_i)+\frac{\partial}{\partial x}(\rho u y_i)=S_{y_i} \qquad 9$$

where y_i denotes mass fraction of species *i* and S_{y_i} the source term of species *i* (for example because of the reaction). S_{y_i} is expressed as

$$S_{y_i}=M_i\gamma_i 1 \qquad 10$$

where M_i denotes the molar weight of species *i* and γ_i the stoichiometric coefficient of the same species. Phenol concentration can be related to fluid density using the following equation.

$$C_{C_6H_6O}=\frac{y_{C_6H_6O}}{M_{C_6H_6O}}\rho \qquad 11$$

where $M_{C_6H_6O}$ denotes the molar weight of phenol, $y_{C_6H_6O}$ the mass fraction of phenol and ρ the density of the reacting medium. First, the above equations must be solved under steady state conditions. Next, the solutions provide the initial boundary conditions for the unsteady model.

2.5. Method of Solution

From the conservation of mass under steady state conditions, it is concluded that ρu is constant. That is also apparent from $\rho u=\frac{\dot m}{A}$, as the mass entry rate and cross section of the reactor are constant. The entrance boundary conditions are the fluid temperature, pressure, mass fraction, and velocity (found from the entrance mass flow rate). The changes of supercritical fluid properties are highly nonlinear and predicting the flow behavior may be considered as a special example of variable property flow modeling. Thus, equations of conservation are coupled and must be solved simultaneously. The set of equations are solved by Euler method. It starts with an initial guess of temperature and the final solution is found via iterations for 101 points in the solution domain. The numerical program is written in MATLAB.

3. Results and Discussion

The model predictions under the conditions where the reactor exchanges heat with the environment are examined first. The results for adiabatic reactors will be presented and discussed next.

3.1. Steady State Conditions

The convective heat transfer between the reactor and the ambience may be stated as $\dot{q} = \frac{H}{d}(T(x) - T_{ext})$.

The parameters H and T_{ext} can either be constant or be functions of temperature or the length of the reactor. Flow conditions have been summarized in Table 2.

Table 2
Flow conditions at the reactor inlet [53].

Inlet Pressure (MPa)	Flow Rate of Waste (l h^{-1})	Phenol Concentration (g l^{-1})	Temperature of Waste (°C)	Flow Rate of Air (g s^{-1})	Temperature of Air (°C)
25	12.5	5	450	3.69	200

3.1.1. Temperature Distribution

Fig. 1 shows the model predictions for temperature variations along the reactor. It can be seen that the temperature decreases all across the flow.

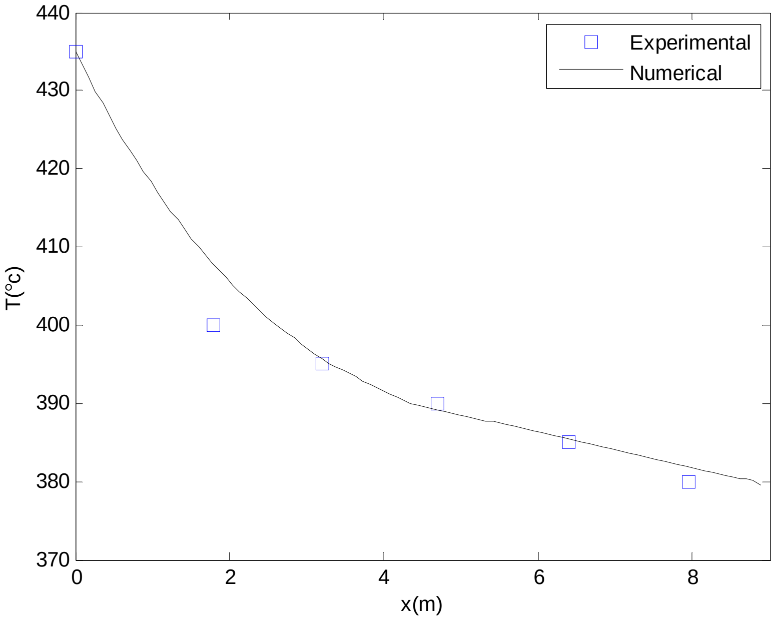

Fig. 1. Experimental data [53] compared with the temperature distribution along the reactor predicted by the present numerical model

This can be a result of slow reaction rate due to low mass fraction of phenol. In this situation, the temperature distribution is more affected by the heat loss from the reactor to the surroundings rather than the heat generated by reaction. Note that the fluid leaves the reactor at 379.57 °C. Both kinetic parameters A and B, introduced in Table 1, have been examined. It is observed that using both set of kinetic parameters yields similar result. Again, the low mass fraction of phenol on one hand and large rate of heat exchange of the reactor with the surroundings on the other hand may explain why the temperatures are not significantly affected by the choice of kinetic parameters.

3.1.2. Waste Mass Fraction

The variation of the mass fraction of phenol along the reactor has been estimated and shown in Fig. 2. The calculations are carried out under steady state conditions with the reactor exchanging heat with the surroundings. It is observed that using kinetic parameters A gives the results closer to the experimental data. The conversion efficiency for kinetic parameters A and B are equal to %68.52 and %87.96, respectively.

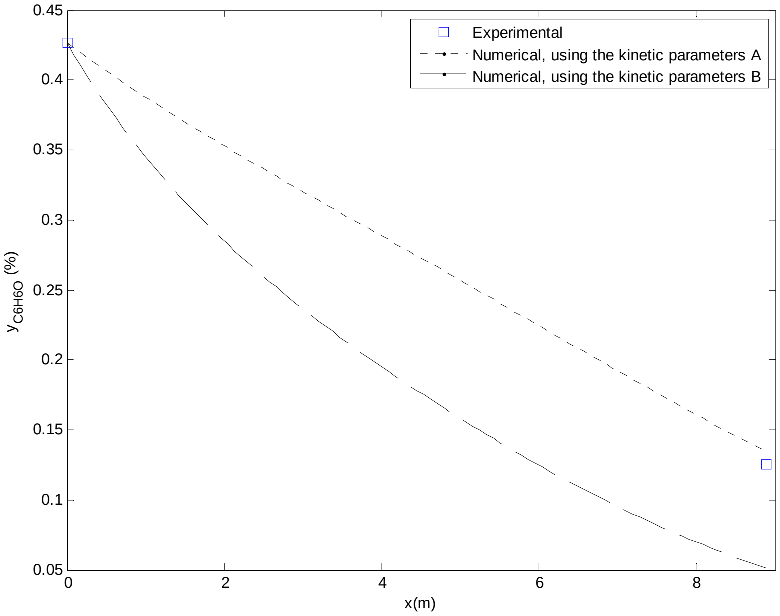

Fig. 2. Experimental data [53] compared with the waste mass fraction distribution along the reactor predicted by the numerical model using the kinetic parameters A and B.

3.1.3. Adiabatic Reactor

The reactor performance under the conditions where there is no heat transfer at the walls $(\dot{q} = 0)$ has been examined in this section. Other flow conditions are the same as before. The model predictions suggest that for adiabatic reactor the temperature remains almost constant. That is because the effective term of heat transfer to the surroundings in the energy equation has been nullified and so the temperature may not decrease. Temperature does not increase significantly in this case either. That is because the rate of reaction is low and the heat released by reaction is almost negligible.

In general, it is a combination of the flow parameters like the reactor diameter and length, mass flux, phenol mass fraction and other conditions at the flow inlet, outside temperature, and most importantly the convective heat transfer coefficient which determines whether the amount of heat generated in the reactor exceeds the heat loss from the walls or not. Since the oxidation of phenol in supercritical water is an exothermic reaction, in an adiabatic reactor the temperature increase in the course of flow, or at the very least it may remain nearly constant if the heat released by the reaction is negligible as is the situation in this case study. Apparently, in a non adiabatic reactor, depending on the flow conditions mentioned above, the fluid temperature may increase, remain constant, or decrease along the reactor.

The variation of waste mass fraction in the adiabatic reactor is however quite noticeable. It is also sensitive to the choice of kinetic parameters. Fig. 3 shows the mass fraction profile for the oxidation of phenol in an adiabatic reactor with kinetic parameters A and B. The conversion efficiency when using kinetic parameters A and B are equal to %58.07 and %86.57, respectively.

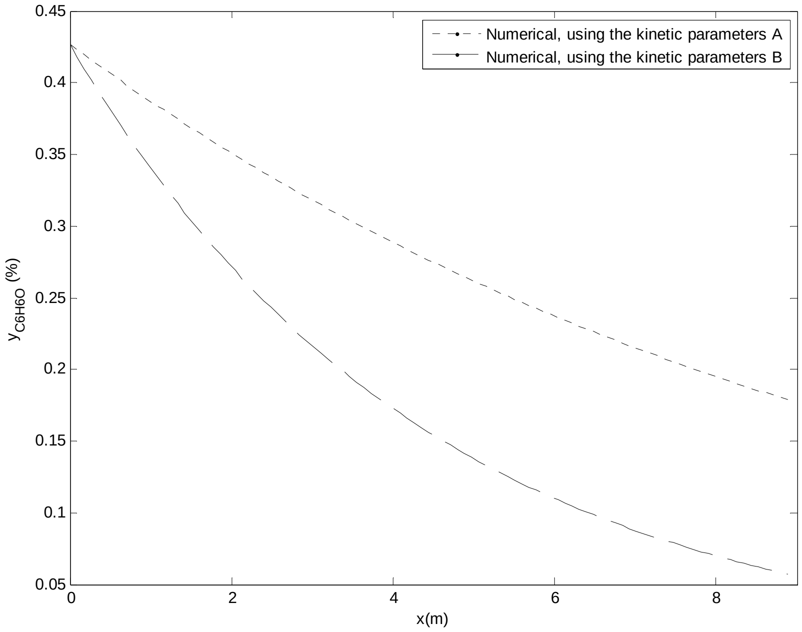

Fig. 3. Waste mass fraction distribution along the adiabatic reactor predicted by the numerical model using the kinetic parameters A and B.

3.2. Unsteady Operating Conditions

Having knowledge about the reactor response to sudden operational changes such as inlet temperature and mass flux can help counter possible hazards and dangers which might occur in practice. Sudden changes in temperature or flow rate can happen at various units and leave behind irreparable effects. As an example, in order to keep the temperature below levels which might cause harm to the equipment and unit, the inlet concentration of wastes may be reduced. Another possible solution would be adding water to the reactor. The present numerical model is employed to examine two situations under which an unsteady state might occur and lead to danger or a loss of control.

3.2.1. Variation of Mass Flow Rate

A change in the inlet mass flow rate can be a result of pump, valve, or other control equipment malfunction. It is worthwhile to examine the reactor response to the occurrence of such a situation via the present numerical code. Fig. 4 depicts an increase of inlet velocity (mass flow rate) to triple the initial value. If the inlet velocity of a steady state reactor triples, the outlet steady state temperature will experience about 18 °C increases. The kinetic parameters A have been used in Fig. 4. Note that this amount of temperature rise lies within the reliable range of temperature variations which the design temperature of the system can handle without leaving any harm to the system.

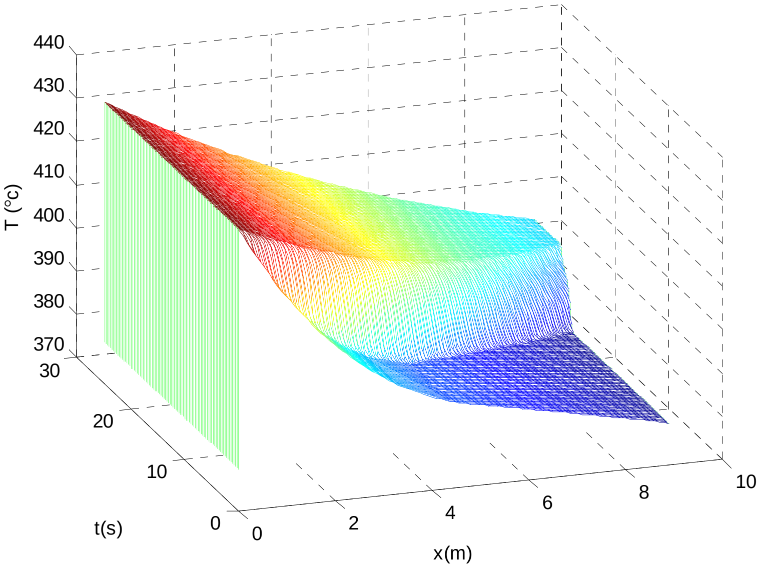

Fig. 4. Temperature distribution at various times along the reactor from the moment when the inlet flow rate has been tripled at t=0 s to the moment of reaching steady state conditions

Fig. 4 is presented in contour form. To better appreciate the results, the graphs of temperature profiles along the reactor for several time intervals are shown separately in Fig. 5. In fact, each curve in Fig. 5 shows the temperature distribution at a particular time. With a sudden increase of inlet velocity, the temperature inside the reactor increases with time.

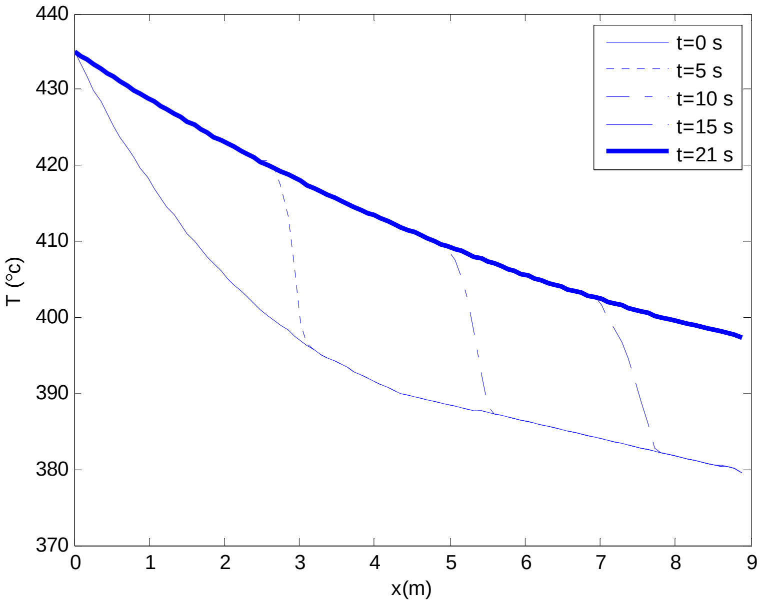

Fig. 5. Temperature variation at various times along the reactor after the inlet flow rate has been tripled.

The temperature distribution presented for unsteady flow conditions in Fig. 4 or Fig. 5, seems to be reasonable. With the sudden increase of the inlet velocity, the residence time within the reactor is decreased. The decrease of residence time means the less opportunity for the flow to exchange heat with the surroundings. It causes the outlet temperature to experience an increase of 18 °C compared to the steady condition before occurrence of the sudden change of mass flux.

Fig. 6 shows mass fraction distribution of phenol along the reactor with time. It is observed that conversion efficiency is reduced with the decrease of residence time. This sounds reasonable as the oxidant and waste have less time to react. The destruction efficiency is dropped from %68.51 to %21.75 when the mass flux triples.

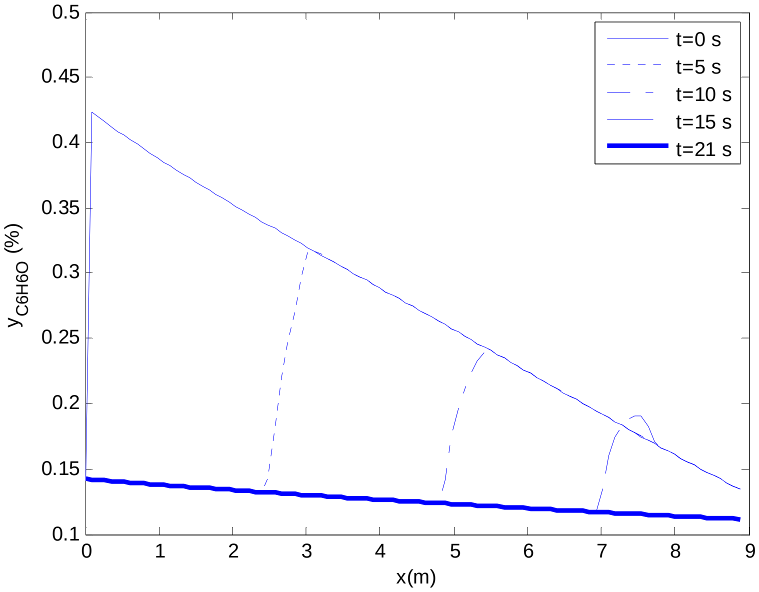

Fig. 6. Mass fraction distribution at various times along the reactor from the moment when the inlet flow rate has tripled at t=0 s to the moment of reaching steady state conditions.

3.2.2. Sudden Increase of Inlet Temperature

One reason for an increase of inlet temperature can be injection of hydrogen peroxide as oxidant in the reactor inlet. Hydrogen peroxide quickly breaks down to water and oxygen and creates heat. If this substance is used as the oxidant, the produced heat results in an increase in the temperature at the inlet of the reactor.

Fig. 7 represents the temperature variations along the reactor as a result of a sudden 10 increase of inlet temperature. As shown, with such a jump of temperature at the inlet, the temperature in the beginning section of reactor is increased compared to original steady state situation. The effect of increase of the inlet temperature is noticeably reduced along the course of flow towards the reactor outlet. The fact that the outlet temperature in this case study is close to the pseudo-critical point plays an important role. The pseudo-critical point is where the specific heat capacity of a supercritical fluid peaks to its maximum value. For water at 25 MPa, the pseudo-critical temperature is around 380 °C. Thus, when the outlet temperature coincides with pseudo-critical temperature, an increase in inlet temperature does not affect the outlet temperature significantly and there is only about 1.5 °C temperature increase in the outlet of reactor.

The overall effect of a sudden increase of 10 °C in inlet temperature is that the rate of waste destruction is slightly decreased from %68.51 to %64.8. This may be appreciated from Fig. 8 where the variations of waste mass fractions are shown for steady state conditions before and after the event of temperature increase at the flow inlet. The increase of inlet temperature gives the impression that the rate of reaction may increase. However, the rise of inlet temperature leads to the decrease of fluid density which, in turn, causes the fluid speed to increase. As discussed in previous section, the enhancement of the fluid speed results in a reduction of destruction efficiency.

It should be noted that there is no experimental data available for the unsteady flow conditions discussed above to validate the model predictions. However, the good agreement of the results with the experiments shown earlier for the steady state flow conditions increases the level of trust with respect to the model predictions for unsteady conditions.

4. Conclusions

In order to better design a supercritical water oxidation unit, it is imperative to be able to predict the variations of the parameters such as temperature and concentration along the reactor under various conditions. In addition, the temperature rise along the reactor should be noted, in order not to cause harm to the constructing materials of the reactor itself. In the present study, a plug flow reactor has been modeled to numerically investigate the oxidation process of phenol in a supercritical water environment under steady and unsteady operating conditions. Some conclusions which may be derived from the current analysis are as follows.

Under steady conditions, the temperature in an adiabatic reactor is higher than a reactor with heat transfer due to the fact that there is no heat transfer with the surroundings in the adiabatic reactor and oxidation of phenol is an exothermic reaction. With respect to the results of the two considered reactors under steady conditions, the non adiabatic reactor is recommended if the waste destruction is of principal importance. Some possible unsteady operational situations which might take place at a supercritical water oxidation reactor have been examined. The results show that the increase of temperature and change in inlet mass flow rate cause alterations in the hydrothermal oxidation unit which are controllable and in a stable range. For instance, for the flow conditions encountered in the current case study, it takes about 81 seconds for the reactor to reach a new steady state condition after a sudden 10 °C rise of the fluid inlet temperature. As another example, it was shown that sudden increase of the flow rate to triple of its initial value causes the fluid to experience about 18 °C temperature increase at the reactor outlet within 21 seconds. Generally, the design temperature of the reactor which takes into consideration the safety factors, supports this range of sudden alterations.

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